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The Effects of Water Spray Cooling in Conjunction with Halogenated Extinguishants on Hydrogen Fluoride Generation and Decay

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Defence Science and Technology Organisation**

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ABSTRACT (U)

The halogenated extinguishants Halon 1301, HFC-227ea (FM200) and NAF-S-III used within Royal Australian Navy vessels for total flooding fire suppression applications have hydrogen fluoride (HF) toxicity concerns. HF is readily produced when these extinguishants are subjected to elevated temperatures and is highly toxic in small concentrations.

In the open literature, water spray used in conjunction with halogenated extinguishants has been reported to reduce peak HF production during extinguishment as well as increasing the HF decay rate. This data is summarised as a function of compartment sizes, type of extinguishant, spray initiation time prior to the extinguishant release, spray duration and the spray application rate. However, the use of water spray in conjunction with halogenated extinguishants still resulted in HF levels above the Occupational Health and Safety workplace maximums and exceeded the Immediate Danger to Life and Health level.

This paper describes the production of HF from halogenated extinguishants and the factors contributing to the amount of HF produced.

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Executive Summary

The halogenated extinguishants Halon 1301, HFC-227ea (FM200) and NAF-S-III used within Royal Australian Navy ships for total flooding fire suppression applications have a number of toxicity concerns, namely cardiac sensitisation issues and the production of thermal decomposition products. Of greatest concern is the formation of hydrogen fluoride (HF) at elevated temperatures. HF is highly toxic, contact with the skin will cause severe burns, eye contact may lead to permanent eye damage including blindness and it may act as a systemic poison.

Halogenated extinguishants are effective in extinguishing Class B liquid fuel fires and they also produce some compartmental cooling. The application of water spray cooling in conjunction with the halogen extinguishant can reduce HF production, significantly reduce compartment temperatures and can 'scrub' HF from the compartment environment. This paper describes HF production from halogenated extinguishants, the factors contributing to the levels of HF produced, typical levels of HF for Class B fires and the reductions in HF as a result of water spray application with the halogenated extinguishant.

The results of studies presented in the open literature have been examined and HF production and decay rates are summarised as functions of type of extinguishant, compartment size, spray initiation, duration of spray and spray application rate.

Water spray cooling used in conjunction with halogenated extinguishants reduces the peak HF concentration and the decay time but the concentrations produced are still above the Occupational Health and Safety workplace maximums and exceed the Immediate Danger to Life and Health (IDLH) level.

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1. Introduction

The use of the halogenated extinguishants Halon 1301, HFC-227ea (FM200) and NAF-S-III in Royal Australian Navy (RAN) vessels for total flooding fire suppression applications will result in the formation of toxic thermal decomposition products. Depending on the extinguishant used, thermal decomposition may produce hydrogen halides, hydrogen cyanide and various halogen gases. Of all the decomposition products, the amount of hydrogen fluoride (HF) produced by the thermal decomposition of halogenated extinguishants during a fire is a major safety concern.

HF is gaseous, toxic in small concentrations, may be fatal if inhaled or swallowed and contact with skin will cause severe burns. Eye contact may lead to permanent eye damage, including blindness and it may act as a systemic poison. In response to the toxicity of HF, compartments in naval ships are evacuated prior to release of these extinguishants. However, a delay in releasing the extinguishant increases the probability of fire growth and therefore the amount of HF produced. The concentration of HF is also dependent on the particular extinguishant and the extinguishing concentration.

This paper summarises current literature and examines how HF is produced by halogenated extinguishants, the factors contributing to the levels of HF produced, typical levels of HF from Class B fires and the reductions in HF as a result of water spray application with the halogenated extinguishants.

2. Halogenated Extinguishants

Table 1 lists the extinguishants used by the RAN, their chemical formulae and design concentrations. The extinguishing concentration is determined from a laboratory test and is the concentration necessary to extinguish a fire with n-heptane as the fuel. The design concentration is determined by adding a 20% safety factor to the extinguishing concentration. The formulae indicate the number of fluorine atoms available per molecule to form HF, while the extinguishant concentration relates to the number of atoms potentially available. However, if the extinguishant concentration used is below the extinguishing concentration, the fire will continue to burn and the extinguishant will continue to thermally decompose increasing the level of HF.

Table 1 The halogenated extinguishants used by the RAN, their formulae, extinguishing and design concentrations and extinguishing mechanism

Extinguishant	Formula	Extinguishing concentration (n-heptane)	Design concentration (n-heptane)	Extinguishing mechanism
Halon 1301	CF_3Br	3.2% [1]	5% [1]	Chemical
HFC-227ea (FM200)	C_3HF_7	6.6% [1]	7.9% [1]	Physical and chemical
NAF-S-III *	$\text{CHClF}_2(82\%)$ $\text{CHClFCF}_3(9.5\%)$ $\text{CHCl}_2\text{CF}_3(4.5\%)$ $\text{C}_{10}\text{H}_{16}(3.75\%)$	9.9% [1]	12.0% [1]	Physical and chemical

* NAF-S-III is a combination of compounds.

Halogenated extinguishants are effective in extinguishing liquid hydrocarbon fuel (Class B) fires, a common fire risk in machinery spaces. They also produce some compartmental cooling for minimising re-flash once the initial fire has been suppressed. The application of water spray with the halogenated extinguishant reduces HF production by faster extinguishment, significantly reducing compartment temperatures and by 'scrubbing' or 'washing' HF from the compartment environment. 'Scrubbing' or 'washing' refers to dissolution of the HF gas in the water spray producing a weak hydrofluoric acid.

3. How is HF produced?

Halogenated extinguishants provide fire suppression through physical and chemical means. The physical means of suppression are (i) thermal, where the heat capacity of the extinguishant gas lowers the flame temperature, reducing the flame /fuel reaction rate and halting the combustion process and (ii) dilution, where the addition of a non-oxygen containing gas slows the combustion reactions by reducing the oxygen-fuel collision frequency. In chemically suppressing combustion, the halogen radicals produced during thermal decomposition of the extinguishant (bromine (Br), fluorine (F) and chlorine (Cl)) remove the active hydrogen, hydroxyl and oxygen radicals (H, OH and O) produced at the flame front during the combustion of hydrocarbon fuels. These active radicals are necessary for the combustion process to continue. However F radicals combine with the H radicals from the combustion process to produce HF which halts the combustion process.

Halon 1301 is the only halogenated extinguishant to suppress fires primarily by chemical means. Upon decomposition, it releases Br radicals which combine with the H radicals

from the fuel breakdown to form HBr. HBr combines with OH radicals to form water and Br radicals which can continue to remove H radicals eventually resulting in fire suppression. However, Halon 1301 also contains fluorine, which combines with the H radicals to form the unwanted HF. Halon 1301 decomposition occurs at temperatures above 480°C.

HFC-227ea extinguishes mainly by thermal means, its high heat capacity reducing the flame temperature below that required for flame propagation when a sufficient quantity is present. HFC-227ea decomposes at temperatures above 400°C producing HF as one of the decomposition by-products.

NAF-S-III also suppresses primarily by thermal means due to its high heat capacity and decomposes at temperatures above 500°C producing HF.

4. Factors affecting the level of HF produced

HF production is dependent on a number of factors including the fire size to compartment volume ratio, extinguishant concentration/extinguishant type and flame contact time. The factors are described below.

- **fire size/compartment volume ratio**

In the same size compartment, higher heat release rate fires have a larger flame area and produce greater concentrations of HF. The compartment size influences the overall concentration where the same amount of HF formed in a larger compartment will result in a lower overall concentration due to the greater volume.

- **extinguishant type/extinguishant concentration**

The type of extinguishant determines the amount of fluorine available while the extinguishant concentration controls the volume of fluorine available to form HF.

- **flame contact time**

The longer the extinguishant is in contact with the flame, the higher the concentration of HF that is formed. Higher flame temperatures also result in greater extinguishant decomposition rates and higher HF concentrations.

The decay rate of HF, that is the rate at which the HF concentration dissipates after formation, is a function of the rate at which the HF reacts with metal surfaces within the compartment.

5. Typical HF concentrations from halogenated extinguishants

The extinguishing times and the HF concentrations produced in a number of different fire scenarios with halogenated extinguishants used in RAN vessels (Halon 1301, HFC-227ea and NAF-S-III) are presented in *Table 2* [2]. The test compartment was a simulated 500 m³ machinery space with a diesel engine mock-up and the compartment remained unventilated during the extinguishant release.

Table 2 shows that the peak HF concentrations are dependent on the extinguishant type but that variations in the extinguishant concentrations used are not significant enough to conclude any trends in behaviour. *Table 2* shows that HFC-227ea and NAF-S-III produce significantly more HF than Halon 1301 irrespective of the fire scenario.

The effect of fire size on HF levels showed no underlying trend, but in general larger fires (in terms of MW) produced greater HF concentrations.

Table 2 Typical HF concentrations for Halon 1301, HFC-227ea and NAF-S-III [2].

Extinguishant	Extinguishant concentration (%)	Fire scenario	Total heat release rate (MW)	Extinguishing times (secs) for each of the fire components				Peak HF (ppm)
				a	b	c	d	
Halon 1301	4.6	2	7.95	15	2	2	n/a	100
	4.8	3B	3.4	5	10	11	n/a	300
	4.7	4	6.0	10	n/a	n/a	n/a	400
HFC-227ea	9.0	2	7.95	13	5	5	n/a	8100
	8.6	2A	2.4	12	2	2	n/a	1500
	8.7	4A	4.75	12	14	2	n/a	3700
	8.8	4	6.0	15	n/a	n/a	n/a	2400
	8.7	3A	3.4	7	9	15	2	5000
	8.1	3B	3.4	3	11	9	n/a	3900
	8.2	3	4.4	4	12	12	n/a	3900
	7.7	2	7.95	9	2	2	n/a	3600
NAF-S-III	11.8	2	7.95	10	3	3	n/a	2500
	10.8	3B	3.4	7	8	14	n/a	2300
	11.8	4	6.0	10	n/a	n/a	n/a	1000
	12.2	2	7.95	1	5	5	n/a	4400
	11.6	3B	3.4	4	4	4	n/a	3400
	10.2	4	6.0	9	n/a	n/a	n/a	9000
	12.7	2A	2.4	11	4	4	n/a	1600
	12.3	3A	3.4	9	15	12	1	5100
	12.3	4A	4.75	11	11	2	n/a	1900

Fire scenario	Fire components	Heat release rate (MW)
2	a. Low pressure heptane spray fire	5.8
	b. High pressure diesel spray fire	1.8
	c. 0.25 m ² heptane pan fire	0.35
2A	a. Low pressure/flow heptane spray fire	0.25
	b. High pressure diesel spray fire	1.8
	c. 0.25 m ² heptane pan fire	0.35
3	a. Low pressure/flow heptane spray fire	1.1
	b. Small wood crib	0.3
	c. 2.0 m ² heptane pan fire	3.0
3A	a. Low pressure/flow heptane spray fire	0.25
	b. Small wood crib	0.30
	c. 0.25 m ² heptane pan fire	0.35
	d. 1.25 m ² heptane pan fire	2.5
3B	a. Low pressure/flow heptane spray fire	1.1
	b. Small wood crib	0.3
	c. 1.25 m ² heptane pan fire	2.0
4	a. 4.0 m ² diesel pan fire	6.0
4A	a. Low pressure/flow heptane spray fire	0.25
	b. 0.25 m ² heptane pan fire	2.0
	c. 1.25 m ² heptane pan fire	2.5

6. Water spray cooling

In sufficient concentration, halogenated extinguishants are effective at extinguishing Class B fires but the HF levels and the temperatures generated by the fires pose a problem for personnel. The intention of water spray cooling used in conjunction with halogenated extinguishants is to enhance fire suppression and improve re-ignition behaviour by reducing compartment temperatures. It also enhances re-entry to the compartment by personnel by reducing peak HF levels and increasing the HF decay rate.

6.1 Spray cooling/extinguishant studies

In the open literature, water spray used in conjunction with halogenated extinguishants has been found to reduce peak HF production during extinguishment, increase the HF decay rate and provide compartment cooling [3,4,5]. These studies examined a number of variables including, spray initiation time, duration of spray and spray application rate. The results, with respect to HF production and decay rate are summarised below as a function of increasing compartment size.

6.1.1 27 m³ compartment [3]

This study comprised a 27 m³ compartment with pan and cascading fires using n-heptane and methanol as fuels and HFC-227ea as the extinguishant. n-heptane and methanol are both challenging to suppression systems as methanol requires high extinguishing concentrations and n-heptane has a flash point of -1°C.

The tests conducted were

- Background tests – fires only
- Pre-burn tests – fires and water spray only
- Baseline tests – fires and HFC-227ea only
- Suppression tests – fires, water spray and HFC-227ea

The water spray system comprised a single nozzle operating at 1035 kPa (150 psi), simulating a shipboard fire main with nozzles producing application rates of between 6.4 and 44.3 litres per minute (lpm) from different nozzle types. The HFC-227ea concentration was 10.6%.

For tests without water spray, the peak HF concentration was 3400 parts per million (ppm) near the flame. The peak HF concentration was reduced when the water spray was discharged 30 seconds prior to the halogenated extinguishant. An increase in the water spray discharge time from 2 minutes to 5 minutes reduced the HF concentration from 55 to 30 ppm, 5 minutes after the HFC-227ea discharge. This compares with 300 ppm at the same time without water spray application, indicating that with water spray, the HF decay is more rapid. Water spray flow rate increases up to 10.6 lpm reduced peak HF concentrations and decay rates.

6.1.2 297 m³ compartment [4]

A 297 m³ compartment with combined pan and cascading 400 kW and 1900 kW methanol and 1900 kW n-heptane fires were used to examine the water spray effect on HF reduction on a HFC-227ea extinguishing system. Fires were given a 60 second pre-burn prior to the extinguishant release and the spray was released 30 seconds prior to the extinguishant.

- *HFC-227ea without water spray:* The larger fires resulted in a higher concentration of HF as a result of larger flame areas. The 1900 kW fires produced higher peak and average HF concentrations compared with the smaller 400 kW fires. The peak HF concentration near the 400 kW methanol fire was 3000 ppm while the peak concentration near the 1900 kW methanol fire was over 18000 ppm. The values after 15 minutes for the 400 kW and 1900 kW methanol fires were 400 ppm and 2000 ppm, respectively.
- *HFC-227ea with water spray:* For the 400 kW fire, continuous application of the water spray, initiated 30 seconds prior to the extinguishant release, reduced the peak HF by approximately one third. The HF concentration also reduced with

time at a faster rate resulting in a significant reduction in HF concentration after 15 minutes. For the 1900 kW methanol fire, the peak HF concentration was 7000 ppm compared with 18000 ppm without water spray and the concentration after 15 minutes was under 100 ppm compared to 2000 ppm without water spray. Similar reductions were obtained with the 1900 kW n-heptane fire; a peak HF concentration of over 7000 ppm was recorded without the water spray which was reduced to approximately 2500 ppm and below 100 ppm after 15 minutes.

6.1.3 370m³ compartment [5]

In this compartment, the fires comprised a diesel pan fire (4.5 MW), diesel spray fires (up to 4.9 MW) and diesel tell-tale fires (51 kW). The compartment volume was 390 m³ and included a gas turbine mock-up reducing the volume to 370 m³. The suppression system was HFC-227ea.

The tests conducted were Background tests – fires only
 Suppression tests – fires and HFC-227ea
 Suppression tests – fires, water spray and HFC-227ea

The water spray system comprised 13 nozzles in an array, running at a system pressure of 550 kPa (80 psi) and a total system application rate of 56 lpm.

The test conducted with the release of HFC-227ea resulted in a peak HF concentration of 5000 ppm; the fire test conducted with the water spray initiated at the same time as the suppressant reduced the peak HF concentration by approximately one half. The water spray initiated prior to the suppressant discharge also reduced the peak HF concentration. The most significant result was a two-minute spray activated 1 minute prior to the extinguishant release where the peak HF concentration was 200 ppm, the peak compartment temperature prior to water activation was 330°C. Other tests showed less success in reducing the HF production. A 3 minutes spray duration activated two minutes prior to the extinguishant release produced a peak HF concentration of 1300 ppm with a peak compartment temperature prior to water spray activation of 190°C. These tests were conducted with a system flow rate of 230 lpm. At a lower flow rate of 150 lpm, released 1 minute prior to the extinguishant for a 2 minute duration, the peak HF was 2000 ppm with a peak compartment temperature before the water spray activation of 270°C. The results of these events are summarised in *Table 3*.

The peak compartment temperatures were reduced significantly after the water spray/extinguishant activation, typically to less than 60°C in seconds.

Table 3. Results of extinguishing events comprising water spray and HFC-227ea in a 370m³ compartment.

Water flow rate	Activation time prior to HFC-227ea	Water spray duration	Peak compartment temperature	Peak HF concentration
(lpm)	(minutes)	(minutes)	(°C)	(ppm)
230	1	2	330	200
230	2	3	190	1300
150	1	2	270	2000

The results in *Table 3* show that water flow rate, the activation time prior to the HFC-227ea release and the duration of the water spray are the controlling parameters in the concentration of HF produced. Higher water flow rates and earlier activation result in greater compartment cooling which will have an effect on the level of HF produced. The spray activated 2 minutes before the HFC-227ea release resulted in greater compartment cooling reducing the vapour generation and oxygen dilution. If oxygen dilution is the controlling extinguishing mechanism, the time to extinguishment will increase as will the concentration of HF.

Comparing the two tests using water flow rates of 230 lpm, the spray released 1 minute prior to the HFC-227ea for two minutes and the spray released 2 minutes prior to the HFC-227ea for 3 minutes, the latter produced a peak compartment temperature of 190°C and the former 330°C. But the lower temperature resulted in less oxygen dilution, delaying extinguishment and a greater HF concentration.

The HF concentrations from similar tests but with different water flow rates indicate that the lower flow rates do not produce sufficient water vapour to reduce the oxygen concentration. Again this will delay extinguishment and contribute to higher HF concentrations.

These results indicate that oxygen dilution is the principal extinguishing mechanism and its effectiveness is reduced as the compartment temperature drops and the water flow rate decreases.

7. Discussion

The HF concentrations produced by the halogenated extinguishants listed in *Table 2* showed peak concentrations up to 9000 ppm. Halon 1301 produced the least amount of HF, with HFC-227ea and NAF-S-III producing significantly greater peak concentrations and thus posing a greater toxicity risk. Water spray cooling used in conjunction with HFC-227ea reduced the peak HF concentration and decay time compared with the extinguishant only system.

Although the concentration of HF produced using the water spray system with HFC-227ea was lower than that produced using the extinguishant only, the levels were still above the Occupational Health and Safety short term (15 minute) exposure limit of 3 ppm [6] and exceed the Immediate Danger to Life and Health (IDLH) level of 30 ppm [6]. This is the concentration below which an individual could endure a 30 minute exposure without experiencing any irreversible health effects. The reduction in HF using water spray does not change the safety protocols associated with the use of the halogenated extinguishing systems and does not significantly lessen the risk associated with their use.

Water spray cooling used with Halon 1301 may result in HF levels lower than IDLH or workplace maximums and further testing would need to be undertaken to confirm this behaviour. However, Halon 1301 is being phased out in the Royal Australian Navy for environmental reasons and further investigation is not intended.

8. Conclusions

The combination of water spray with FM200 or NAF-S-III will not reduce the HF concentration below the short term exposure or ILDH levels. Water spray therefore provides no risk reduction associated with exposure to HF during the initial breakdown of the extinguishant when peak levels are recorded.

The HF produced during water spray application with the halogenated extinguishants will have lower peak levels and will dissipate more quickly than if the water spray were not used. This behaviour would be beneficial during operational procedures where reduced re-entry times into affected compartments would result in faster capability recovery.

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